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Microwave spectrum of chlorobenzene

By HANS SELÉN

The microwave spectrum of $C_6^{12}H_5Cl^{35}$ in the K-band region has been reported previously by Erlandsson (1). The absorption frequencies were then measured with a cavity wave-meter, and the quadrupole splittings were not resolved. In the present investigation a larger frequency region has been studied, a frequency standard has been used for the measurements, and the hyperfine structure has been investigated. The greater number of lines and the improved accuracy has resulted in better values for the rotational constants. The values of B and C are in essential agreement with Erlandsson's results, while a slightly different value of A has been obtained.

Table 1.

Transition	Observed frequency	Center frequency of doublet	Calculated frequency	Doublet-splitting	Quadrupole coupling constant $\|eQq\|$
4_{04}—5_{05}	13660.4		13660.3		
4_{14}—5_{15}	13112.6		13111.7		
4_{13}—5_{14}	14811.6		14811.8		
4_{23}—5_{24}	14005.4 14008.3	14006.9	14006.6	2.9	58
4_{22}—5_{23}	14398.3 14401.8	14400.1	14398.5	3.5	69
5_{05}—6_{06}	16210.3		16210.4		
5_{15}—6_{16}	15689.2		15688.5		
5_{14}—6_{15}	17705.8		17705.2		
5_{24}—6_{25}	16769.3 16771.2	16770.3	16770.3	1.9	67
5_{23}—6_{24}	17421.0 17423.0	17422.0	17422.0	2.0	68
5_{33}—6_{34}	16954.9 16959.3	16957.1	16955.9	4.4	68
5_{32}—6_{33}	16996.5 17001.3	16998.9	16998.8	4.8	74
6_{06}—7_{07}	18702.2		18702.1		
6_{16}—7_{17}	18246.7		18246.2		
6_{15}—7_{16}	20554.7		20554.0		
6_{25}—7_{26}	19513.4		19513.8		
6_{24}—7_{25}	20482.4		20482.2		
6_{34}—7_{35}	19797.9 19800.7	19799.3	19799.7	2.8	69
6_{33}—7_{34}	19893.5 19895.8	19894.7	19894.7	2.3	57

Table 1 (*continued*)

Transition	Observed frequency	Center frequency of doublet	Calculated frequency	Doublet-splitting	Quadrupole coupling constant |eQq|
7_{07}—8_{08}	21157.0		21155.7		
7_{17}—8_{18}	20785.9		20785.6		
7_{16}—8_{17}	—		23346.2		
7_{26}—8_{27}	22233.8		22234.5		
7_{25}—8_{26}	23554.7		23554.8		
7_{35}—8_{36}	22644.0		22643.6		
7_{34}—8_{35}	22829.2		22829.0		
8_{08}—9_{09}	—		23591.3		
8_{18}—9_{19}	23308.6		23308.7		
8_{17}—9_{18}	—		26069.9		
8_{27}—9_{28}	24928.7		24930.1		
8_{26}—9_{27}	—		26614.3		
8_{36}—9_{37}	25483.6		25483.4		
8_{35}—9_{36}	25810.9		25811.0		
8_{45}—9_{46}	25483.6 25485.9	25484.8	25484.9	2.3	69
8_{44}—9_{45}	25502.0 25504.2	25503.1	25503.7	2.2	65

The lines measured (Table 1) arise from transitions $\Delta J = 1$ with J-values ranging from $J = 4$ to $J = 9$. From the theory of quadrupole moment splittings given by Bragg and Golden (2) it was found that such lines having low values of K_{-1} should have essentially a narrow doublet structure with the splitting increasing with K_{-1}. For higher K_{-1}-values the splittings should be more complex. In agreement with this it was found that the lines having the lowest values of K_{-1} could not be resolved. Lines with intermediate K_{-1} showed a narrow doublet structure. For the higher K_{-1} the splittings are sufficiently complex to make the identifications uncertain. In addition it seems doubtful whether the first order theory for the splittings holds for these lines. They have therefore been omitted from the analysis.

The evaluation of the rotational constants has been based on the unresolved lines and the center frequencies of the doublets. The calculations were carried out with the aid of the computing machine BESK using the programs described in (3) and (4). The following values were obtained

$$A = 5.67997 \quad B = 1.57687 \quad C = 1.23361 \text{ kMHz} \quad \varkappa = -0.8456$$

Frequencies calculated from these constants agree with observed values to about ± 1 MHz with a maximum error of 1.6 MHz. The rather large errors are due to the line widths which may amount to several MHz and limit the accuracy of measurements.

In the evaluation of the quadrupole coupling constant eQq it was assumed that the field around the Cl-nucleus has rotational symmetry around the C–Cl bond. The average value for all doublets is 66.4 MHz with individual variations between 56 and 74 MHz (see Table 1). The result may be compared with the value 69.24 obtained by Livingstone (5) from pure quadrupole resonances in solid chlorobenzene.

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